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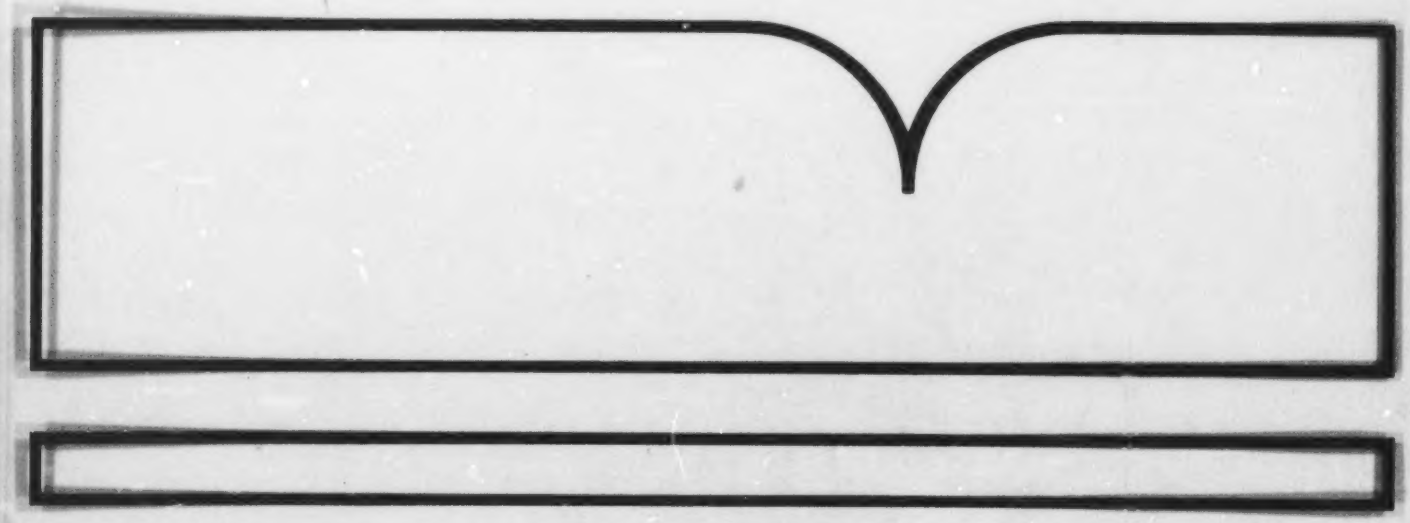

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DETERMINATION OF AMBIENT AIR HYDROCARBONS IN 39 U. S. CITIES

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INTRODUCTION

The ozone forming potential of an air mass is a strong function of the nonmethane organic compounds (NMOC)-to-nitrogen oxides (NOx) ratio. Reduction of this ratio by reducing NMOC emissions is believed to be the most effective means for reducing ozone levels in urban areas (1-2). Local pollution agencies use photochemical computer models to forecast the necessary NMOC reductions to achieve desired ozone concentrations. These models require as input accurate local ambient NMOC and NOx concentrations to achieve confident results. Recent EPA research has led to the development of a much more accurate and precise method for NMOC measurement than was previously available with commercial analyzers. The new method, a simplification of the gas chromatographic (GC) speciation technique without a GC column, uses cryogenic concentration of the air sample to yield an enhanced flame ionization detector (FID) response, and is referred to as the preconcentration-direct flame ionization detection (PDFID) method (3-4).

Currently in the U.S. more than 60 urban areas are not in compliance with the National Ambient Air Quality Standard for ozone (5). In 1984 the EPA Office of Air Quality Planning and Standards (OAQPS) began an assistance program designed to determine NMOC in participating non-attainment cities using the new PDFID method. To further minimize potential sources of sampling and analysis error and to assure consistently high quality measurements, air samples were collected in electropolished stainless steel (ss) canisters for analysis at a central laboratory. As part of this project the Atmospheric Sciences Research Laboratory (ASRL) of the EPA analyzed 10 to 20% of the samples to determine the speciated hydrocarbon composition. Over 800 samples from 39 cities were analyzed from 1984 through 1986.

EXPERIMENTAL METHODS

Sampling was daily excluding weekends from 6 to 9 am, June through September of each year. Ambient air was pumped into electropolished, 6-L, ss spheres and air freighted to Research Triangle Park for analysis. The sampling methodology is described in detail elsewhere (5-7). Table I lists the cities sampled with corresponding number of samples by year.

Two gas chromatographic analyses were performed on each sample: C_2 to C_{12} hydrocarbons were separated on a fused silica capillary column. The C_2 hydrocarbons, which could not consistently be resolved on our 60-m capillary column, were separated on a 2-m, 3.2-cm o.d. ss column packed with 60-80 mesh grade 58 silica gel (Grace Laboratories). The packed column was temperature programed from 45°C, held for 5 min, to 60°C at 10°C/min. The analysis parameters for the capillary column are

shown in Table II.

For both analyses, 500-ml of sample air was preconcentrated using liquid argon (-186°C) prior to injection and GC separation. The cryogenic trap for the capillary analysis is described in Table II. The trap for the packed column analysis was a 26-cm by 3.2-mm o.d. ss tube packed with Carbowax 20M on 80-100 mesh Chromosorb W-AW. The samples were injected by desorption through the trap (front-flush) at room temperature for one minute. Front-flushing the trap prevented water and heavier hydrocarbons from entering the silica gel column. The cryogenic traps for both GC analyses were back-flushed with carrier gas to remove traces of water and heavy organics between analyses.

In the first year of the study both analyses were performed on a Hewlett-Packard HP-5880A GC equipped with dual FIDs. In 1985, to speed the time required to analyze a sample, the C_2 determination was installed on a Perkin Elmer sigma 2B GC. In 1984 and 1985 both determinations employed a dual six-port valve configuration designed to route samples through the cryogenic trap, to inject the trap contents onto the column, or to back-flush the trap with helium. In 1986 the capillary analysis was changed to a one valve configuration with toggle valves used to determine back-flush versus trapping mode for the capillary analysis.

During the 1987 study detailed GC-FID/GC-mass spectrometric (MS) analyses were performed by Battelle-Columbus Laboratories for 17 selected samples. The GC and MS were Hewlett-Packard models HP5880A and HP5970 respectively. The analysis parameters for the Battelle GC-MS/FID analysis are also listed in Table II.

RESULTS AND DISCUSSION

The limits of detection (LOD) and quantification (LOQ) were estimated using the method described by Knoll (8). The LOD and LOQ were 0.04 and 0.12 parts-per-billion as carbon (ppbC), respectively. These values are a function of the sample amount injected onto the column; however, they remain constant for all GC peaks regardless of retention time.

All of the peaks were quantified using a per carbon response factor determined from a 3 ppm propane-in-air standard reference material (SRM 1665b) from the National Bureau of Standards. The assumption herein, that FID response for all hydrocarbons is identical, is not quite correct; but, it is not far wrong. The work of Dietz (9) shows that the relative FID response for a large number of paraffins, olefins, and aromatics is about +/- 10%. It would be very time consuming to make standards for even the most abundant 30 or 40 compounds, and we could not consistently produce ppb or ppm standards significantly better

than +/- 10% accuracy.

The quantitative precision of our capillary column method was determined by calculating individual peak coefficients of variation (CV) for 12, 1984 duplicate determinations. The results showed that CV decreased (precision increased) as concentration increased. CV for concentrations >5 ppbC were typically less than 15%. However for concentrations <1 ppbC CV ranged from 10 to 95%. No relationship was observed between concentration precision and retention time, which indicated that quantitative precision was the same for all peaks.

A cylinder mixture of propane-in-air was analyzed on a near daily basis as a QA measure to determine the variation of FID response over time. The variation of the daily propane response (% deviation from initial response for each year) over the 1984 to 1986 period was approximately +/- 12%.

Retention time identifications were determined by a combination of the following: 1) Analysis of known hydrocarbons prepared by syringe injection into Tedlar bags filled with air. 2) Reference to the chromatography literature retention times for non-polar columns such as SF-96, OV1101 and SE-30 (10). This was particularly useful for determining the order of elution. 3) Comparison to retention time results of other investigators such as Papa, et al. (11), Nelson and Quigley (12), and Hayes and Pitzer (13). 4) Two precolumn strippers removed olefins and olefins plus aromatics from ambient samples (14). This was useful for both the confirmation of identified peaks and the determination of unidentified peaks as paraffin, olefin, or aromatic. Usually one pair of stripper column analyses were performed per site per year. 5) GC-MS/FID analysis of selected samples.

The HP-5880 GC names peaks according to a user-created calibration table of retention times, unique calibration numbers for each peak (0 to 511), and an optional peak name. A retention index system based on user-identified reference peaks (up to 10) corrects for shifting retention times. A match is obtained if the corrected retention time falls within a calibration table retention window which consists of each retention time +/- a user-specified tolerance percentage (one for all reference peaks and one for non-reference peaks). Our experience was that this method for naming peaks worked well for the complex organic compound mixture found in ambient air. A GC calibration table was prepared that identified 314 peaks by a calibration number. The table consisted of 97 peaks specifically named, 214 identified by carbon number and bond type (olefin, paraffin, or aromatic), and 3 labeled unknown . Table III shows the 97 peaks that have been specifically identified on our capillary analysis and indicates those confirmed by MS. It also gives the mean retention time with standard deviation determined from the 1986

results. Figure 1 shows a typical sample chromatogram with some of the peaks identified.

Since retention times are used for identifying peaks, it follows that retention time precision is important. The standard deviations for the 113 most frequently observed peaks were determined and plotted versus the mean retention times in Figure 2. The retention time standard deviation is not constant: it rises from 0.02 min at 11 min to a peak of 0.07 min in the 16 min area and then declines gradually back down to 0.02 min at about 24 min. This effect may be due to water condensation at -50°C and subsequent evaporation during the temperature program. Previously an even greater variability had been observed until a 23-cm piece of 1/16-in o.d. ss tube was introduced inside the oven to connect the column to the sampling/injection valve. Apparently, with this modification, the water condenses on the walls of the ss tube rather than the column itself where it can restrict the carrier gas flow.

Seventeen samples were analyzed by GC-MS/FID by Battelle-Columbus Laboratories in 1987. As Table II shows the GC-MS/FID column and analysis conditions were similar enough to ours that a confirmation of the more abundant peaks could be obtained. Peak comparisons after 25 min were not attempted since column temperature program rates after 25 min for the two analyses were significantly different. Samples for GC-MS/FID were selected to identify large, atypical concentration peaks as well as to confirm the identification of peaks observed in a typical sample. A level 2 confirmation (15) was obtained for 40 of the peaks in Table II by matching both retention times and MS spectra, as determined by the spectrometer's computer search of the EPA/NIH MS library. A tailing peak commonly observed between iso- and n-pentane was identified as acetone. Other uncommon peaks observed in some samples were methylchloroform, chlorodifluoroethane (Freon-22), chlorobenzene, dichlorobenzene, methylfluoride, ethylacetate, and isopropylacetate.

Two particularily vexing problems encountered with the capillary analysis during this study should be mentioned. The connection between the capillary column and the 1/16-in ss inlet tube was susceptable to leakage especially at subambient temperature. A standard chromatographic fitting (Swagelok) with a vespel/40% graphite ferrule connected the fused silica column to the ss inlet tube. The leak that resulted apparently from material contraction at -50°C would close when the oven reached room temperature, making diagnosis difficult. A commerically available chromatographic fitting (Valco) specifically designed to accept a 0.5-mm o.d. capillary column at one end and a 1/16-in o.d. tube at the other significantly reduced the column leak problem. The connection integrity was tested by analyzing our daily propane QA standard at both -50°C and at room temperature.

If the results were within about 1%, the connection was deamed leak-tight.

The other problem resulted from removal of the GC manufacturer's chemical scrubber installed between the carrier gas flow controller and the inlet valves "to remove any bleed of plasticizers, etc. from the flow controller diaphragms" (16). We found that when the scrubber was removed, contamination--denoted by a particularily large peak at 23 min--was observed in the chromatograms. This problem was difficult to diagnose, because the contamination peak's appearance and magnitude were inconsistent: it would be present in the first few samples of a day, disappear for the remainder of the day, and reappear the next day. It did not appear at all if water was not present in a sample. Thus analysis of dry zero air did not give an accurate system blank. To avoid this contamination the scrubber had to be in place and periodically reconditioned by heating under carrier flow (16).

A statistical summary of the concentration results for the 48 most abundant peaks for all samples from 1984-1986 are shown in Table IV. The table lists compounds in descending order of abundance with their corresponding concentration range statistics, which are number of samples (n), median concentration in ppbC, minimum concentration (min.), twenty-fifth (25%) and seventy-fifth (75%) percentile concentrations, and maximum (max.) concentration. The 48 compounds consisted of 25 paraffins, 15 aromatics, 7 olefins, and acetylene. Three of the aromatics were not specifically identified. The sum of median concentrations for the paraffins, 266 ppbC, represented 60% of the total for the 48 compounds. Aromatics, 116 ppbC, were 26%; olefins, 46.8 ppbC, were 11%; and acetylene, 12.9 ppbC, was 2.7%.

CONCLUSIONS

During the period 1984-1986, over 800 ambient air samples from 39 urban areas in the U. S. were analyzed by capillary GC-FID with sample cryogenic preconcentration. A table of 314 peaks identified by retention time and number was used to identify the peaks of each sample. The number of peaks per sample ranged from 50 to over 200. GC-MS/FID was used to confirm 40 peak identifications and to identify the presence of oxygenated, chlorinated, and fluorinated hydrocarbons in some samples. The overall compound order of abundance by concentration (ppbC) was paraffins followed by aromatics and olefins.

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Table II. GC-FID and GC-MS/FID Analysis Parameters

Parameter	Laboratory	
	EPA/ASRL	Battelle-Columbus
Analysis	GC-FID	GC-MS/FID
Column	DB-1 fused silica	HP-ULTRA-1 fused silica
Length	60-m	50-m
I.D.	0.32 mm	0.32 mm
Film tnickness	1.0 um	0.52 um
Liquid thickness	cross-linked methylsilicone	cross-linked methylsilicone
Column manufacturer	J&W Scientific	Hewlett-Packard
Carrier gas	Helium	Helium
Temperature Program		
initial	-50°C	-50°C
rate	8°C/min	8°C/min
final	200°C	150°C
post rate	None	30°C/min
post temperature	None	200°C
Sample size	500 ml	800 ml
Cryogenic trap	1/8-in o.d. ss tube	1/8-in o.d. ss tube
length	20-cm	20-cm
packing	60-80 mesh glass beads, untreated	60-80 mesh glass beads, treated
cryogen	liquid argon	liquid N_2, -150°C
desorption	hot water, 90°C	150°C
GC manufacturer/model	HP-5880A	HP-5880A/HP5970
Detectors	FID	FID/MSD

Table I. Cities where NMOC samples were collected.

EPA Region	City	Number of Samples 1984	1985	1986
I	Boston MA		8	
	Portland ME		13	0
II	New Haven CT			16
	Bridgeport CT			16
	Bronx NY			16
	Manhattan NY			12
	Trenton NJ			16
III	Baltimore MD			7
	Scranton PA	9		
	Philadelphia PA (2)*	7	24	14
	Washington DC	10	11	11
	Richmond VA	10	14	
IV	Atlanta GA	7		14
	Birmingham AL	6		13
	Charlotte NC	16		
	Chattonooga TN	12		
	Memphis TN	8		
	Miami FL	3		
	West Palm Beach FL	8		
V	Akron OH	10		
	Cincinnati OH	7		
	Cleveland OH		17	
	Indianapolis IN	10		
	Chicago IL (2)			22
VI	Beaumont TX	9	19	13
	Clute TX	10	17	
	Dallas TX	13	23	14
	El Paso TX	8	17	9
	Fort Worth TX	13	19	16
	Houston TX (2)		22	26
	Texas City TX	13	15	
	West Orange TX	16	16	
	Baton Rouge LA		16	
	Lake Charles LA		16	
	Tulsa OK			12
VII	Kansas City MO	11	18	
	St. Louis MO		18	
	Denver CO (2)			25
	Salt Lake City UT (2)			27

*Number of sites if >1 are in parantheses.

Table III. Peak Identification Table

RT, min	SD, min	Calib. Number	MS Confirm	Compound
1.841	0.017	102		ETHYLENE
1.887	0.014	103		ACETYLENE
1.948	0.022	101		ETHANE
2.919	0.020	104		PROPYLENE
3.022	0.019	105		PROPANE
4.995	0.013	110	YES	ISOBUTANE
6.001	0.339	113	YES	2-METHYLPROPENE,BUTENE-1
6.217	0.070	114		1,3-BUTADIENE
6.347	0.013	115	YES	n-BUTANE
6.844	0.042	116	YES	t-2-BUTENE
7.396	0.016	117	YES	c-2-BUTENE
8.621	0.016	118		3-METHYL-1-BUTENE
9.275	0.017	119	YES	ISOPENTANE
9.888	0.018	121		1-PENTENE
10.159	0.018	123	YES	2-METHYL-1-BUTENE
10.291	0.018	124	YES	n-PENTANE
10.428	0.610	125	YES	ISOPRENE
10.625	0.022	126	YES	t-2-PENTENE
10.986	0.023	128	YES	2-METHYL-2-BUTENE
11.057	0.026	129	YES	c-2-PENTENE
11.540	0.033	133	YES	2,2-DIMETHYLBUTANE
12.369	0.046	137		4-METHYL-1-PENTENE
12.478	0.043	138	YES	CYCLOPENTANE
12.623	0.049	139	YES	2,3-DIMETHYLBUTANE
12.701	0.050	140		c-4-METHYL-2-PENTENE
12.822	0.054	141	YES	2-METHYLPENTANE
12.904	0.056	142		t-4-METHYL-2-PENTENE
13.299	0.055	145	YES	3-METHYLPENTANE
13.511	0.057	146		2METHYL1PENTENE,1HEXENE
13.924	0.063	148	YES	n-HEXANE,2-ETHYL-1-BUTENE
14.180	0.063	151		2-METHYL-2-PENTENE
14.402	0.066	153		c or t-2-HEXENE
14.611	0.063	155		c&t-3-METHYL-2-PENTENE
14.740	0.058	156	YES	METHYLCYCLOPENTANE
14.949	0.064	157	YES	2,4-DIMETHYLPENTANE
15.032	0.059	158		2,2,3-TRIMETHYL-1-BUTENE
15.542	0.059	162	YES	BENZENE
15.730	0.064	163	YES	3,3-DIMETHYLPENTANE
15.818	0.055	164	YES	CYCLOHEXANE
16.183	0.059	166	YES	2-METHYLHEXANE
16.214	0.062	167	YES	2,3-DIMETHYLPENTANE
16.281	0.060	168		CYCLOHEXENE
16.454	0.056	170	YES	3-METHYLHEXANE
16.870	0.054	173	YES	2,2,4-TRIMETHYLPENTANE

Table III. Continued.

RT, min	SD, min	Calib. Number	MS Confirm	Compound
17.222	0.052	175	YES	n-HEPTANE
17.366	0.053	176		t-HEPTENE-2
17.616	0.050	178		c-HEPTENE-2
17.830	0.046	179	YES	METHYLCYCLOHEXANE
18.211	0.048	180		2,5-DIMETHYLHEXANE & 3-METHYLCYCLOHEXENE
18.281	0.046	181		2,4-DIMETHYLHEXANE
18.889	0.042	185	YES	TOLUENE
19.237	0.041	189	YES	2-METHYLHEPTANE
19.458	0.039	191	YES	3-METHYLHEPTANE
19.771	0.037	193		2,2,5-TRIMETHYLHEXANE
19.856	0.037	194		1-OCTENE
19.951	0.028	195		CYCLOHEPTANE
20.204	0.036	198	YES	n-OCTANE
20.517	0.036	201		c-2-OCTENE
20.878	0.035	204		2,4-DIMETHYLHEPTANE
21.128	0.022	208		ETHYLCYCLOHEXANE
21.237	0.030	209		2,5-DIMETHYLHEPTANE
21.612	0.029	213	YES	ETHYLBENZENE
21.694	0.024	214		2,3-DIMETHYLHEPTANE
21.846	0.029	215	YES	m&p-XYLENE
22.004	0.028	216		4-METHYLOCTANE
22.194	0.027	218		3-METHYLOCTANE
22.474	0.028	222	YES	o-XYLENE
22.616	0.028	224		1-NONENE
22.907	0.023	228	YES	n-NONANE
23.323	0.023	232		ISOPROPYLBENZENE
23.868	0.030	239		a-PINENE
24.085	0.024	242	YES	n-PROPYLBENZENE
24.259	0.024	244	YES	m-ETHYLTOLUENE
24.322	0.025	245	YES	p-ETHYLTOLUENE
24.480	0.033	247		4-METHYLNONANE
24.723	0.023	249	YES	o-ETHYLTOLUENE
25.029	0.058	252		p,m,o-METHYLSTYRENE
25.092	0.024	253	YES	1,2,4-TRIMETHYLBENZENE
25.394	0.022	256	YES	n-DECANE
25.526	0.017	258		sec-BUTYLBENZENE
25.690	0.023	408		delta-3-CARENE
25.787	0.018	260	YES	1,2,3-TRIMETHYLBENZENE
25.843	0.035	261		1-METHYL-4-ISOPROPYLBENZENE
26.383	0.019	266		1,3-DIETHYLBENZENE
26.589	0.018	268		1,4-DIETHYLBENZENE
26.693	0.018	270		1,2-DIETHYLBENZENE
27.056	0.020	275		2,6-DIMETHYLSTYRENE
27.105	0.024	276		1,2-DIMETHYL-4-ETHYLBENZENE

Table III. Continued.

RT, min	SD, min	Calib. Number	MS Confirm	Compound
27.686	0.021	282		1,2-DIMETHYL-3-ETHYLBENZENE
27.910	0.045	284		1,2,4,5-TETRAMETHYLBENZENE
27.997	0.019	285		1,2,3,5-TETRAMETHYLBENZENE
28.097	0.047	287		ISOAMYLBENZENE
28.797	0.024	294		1,2,3,4-TETRAMETHYLBENZENE
28.924	0.044	380		N-AMYLBENZENE
31.089	0.117	316		N-HEXYLBENZENE

Table IV. Concentration* statistics for most abundant compounds.

N	Median	Min.	25%	75%	Max.	Compound
832	45.3	1.4	26.2	71.6	3393	ISOPENTANE
833	40.3	4.5	23.9	65.5	5448	n-BUTANE
836	33.8	2.7	20.6	56.6	1299	TOLUENE
835	23.5	1.8	12.2	45.2	393	PROPANE
830	23.3	0.6	12.4	41.0	475	ETHANE
834	22.0	1.0	12.5	36.0	1450	n-PENTANE
707	21.4	1.2	13.2	35.8	1001	ETHYLENE
836	18.1	1.3	11.3	30.0	338	m&p-XYLENE
836	14.9	1.2	8.5	23.5	647	2-METHYLPENTANE
835	14.8	1.4	8.4	28.6	1433	ISOBUTANE
709	12.9	0.0	7.3	23.2	114	ACETYLENE
835	12.6	1.0	7.9	19.9	273	BENZENE
836	11.0	0.8	6.2	18.4	601	n-HEXANE,2-ETHYL-1-BUTENE
831	10.7	0.1	6.4	16.6	351	3-METHYLPENTANE
828	10.6	0.0	6.7	17.1	81	1,2,4-TRIMETHYLBENZENE
835	7.7	0.4	4.3	14.3	455	PROPYLENE
763	7.3	0.2	4.5	11.7	173	2-METHYLHEXANE
831	7.2	0.9	4.7	11.6	79	o-XYLENE
835	6.8	0.4	3.9	11.6	106	2,2,4-TRIMETHYLPENTANE
834	6.4	0.5	3.7	10.3	293	METHYLCYCLOPENTANE
828	5.9	0.3	3.5	9.7	168	3-METHYLHEXANE
827	5.9	0.0	3.8	9.8	365	2-METHYLPROPENE,BUTENE-1
836	5.9	0.7	3.6	9.8	159	ETHYLBENZENE
832	5.3	0.1	3.3	8.6	83	m-ETHYLTOLUENE
831	4.7	0.1	2.8	8.2	233	n-HEPTANE
834	3.8	0.3	2.3	6.1	177	2,3-DIMETHYLBUTANE
750	3.6	0.0	1.9	6.0	339	c-2-PENTENE
758	3.4	0.1	1.6	5.7	1701	1,2,3-TRIMETHYLBENZENE
836	3.4	0.3	2.0	6.0	184	METHYLCYCLOHEXANE

Table IV. Continued.

N	Median	Min.	25%	75%	Max.	Compound
835	3.3	0.2	1.9	6.0	138	n-DECANE
825	3.0	0.3	2.0	5.1	51	C9 AROMATIC
773	3.0	0.2	1.8	4.7	71	C11 AROMATIC
807	2.9	0.1	1.5	4.7	291	t-2-PENTENE
836	2.9	0.2	1.9	4.6	54	o-ETHYLTOLUENE
831	2.8	0.1	1.8	4.7	54	p-ETHYLTOLUENE
832	2.8	0.2	1.8	4.5	235	C10 AROMATIC
799	2.6	0.2	1.6	4.6	163	n-OCTANE
822	2.6	0.1	1.4	4.4	242	2-METHYL-1-BUTENE
756	2.5	0.2	1.6	4.3	149	1,2-DIMETHYL-3-ETHYLBENZENE
811	2.5	0.1	1.4	4.2	377	t-2-BUTENE
833	2.5	0.1	1.5	4.4	78	2,3,4-TRIMETHYLPENTANE
820	2.5	0.1	1.3	4.2	75	2-METHYLHEPTANE
821	2.4	0.1	1.5	4.0	33	1,4-DIETHYLBENZENE
832	2.2	0.1	1.4	3.9	109	3-METHYLHEPTANE
821	2.2	0.2	1.3	4.2	89	n-NONANE
817	2.2	0.2	1.1	4.8	409	CYCLOHEXANE
827	2.2	0.2	1.3	3.8	72	2,4-DIMETHYLPENTANE
823	2.1	0.1	1.2	3.2	104	CYCLOPENTANE

* All concentrations are parts-per-billion as carbon.

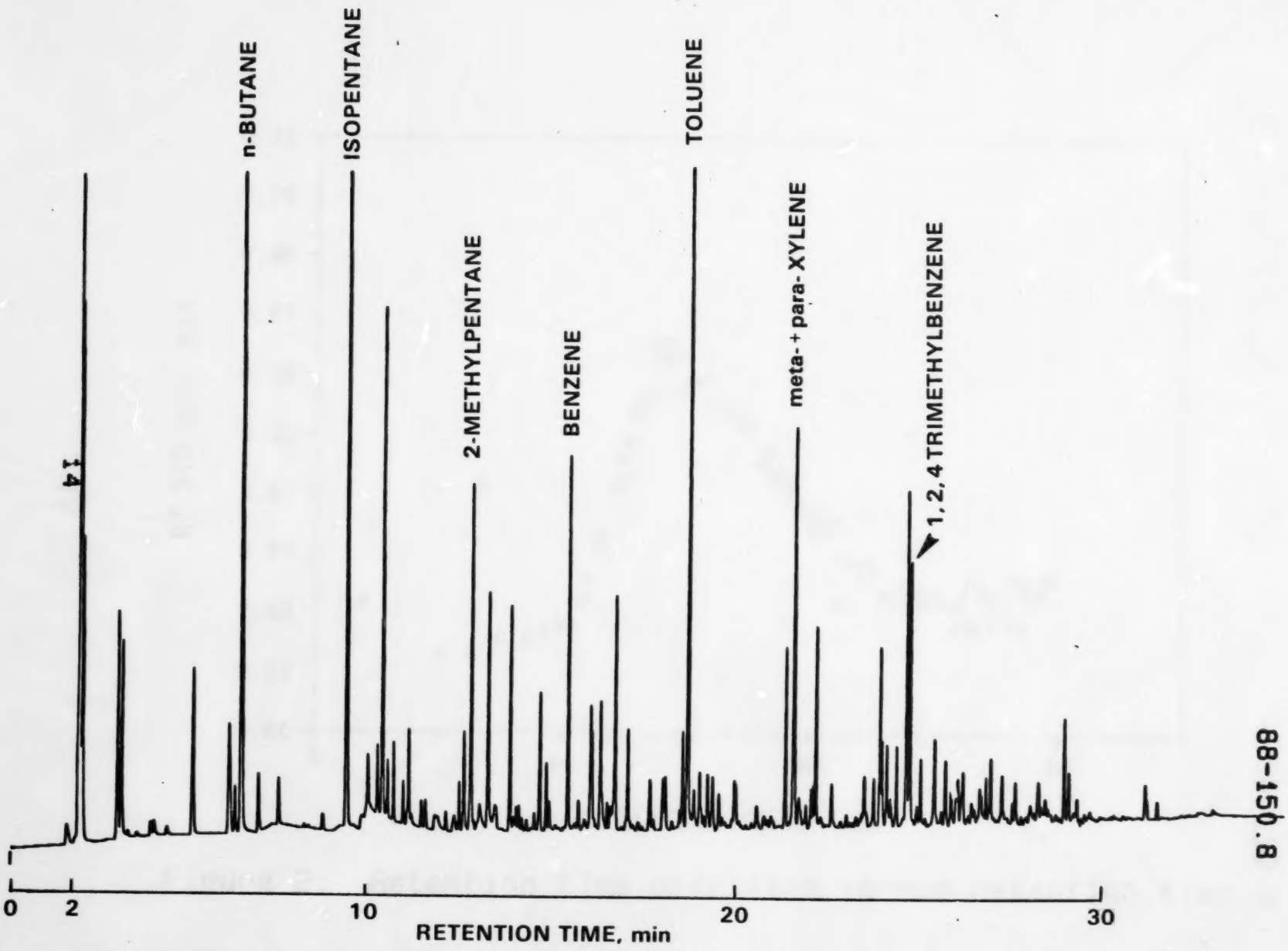
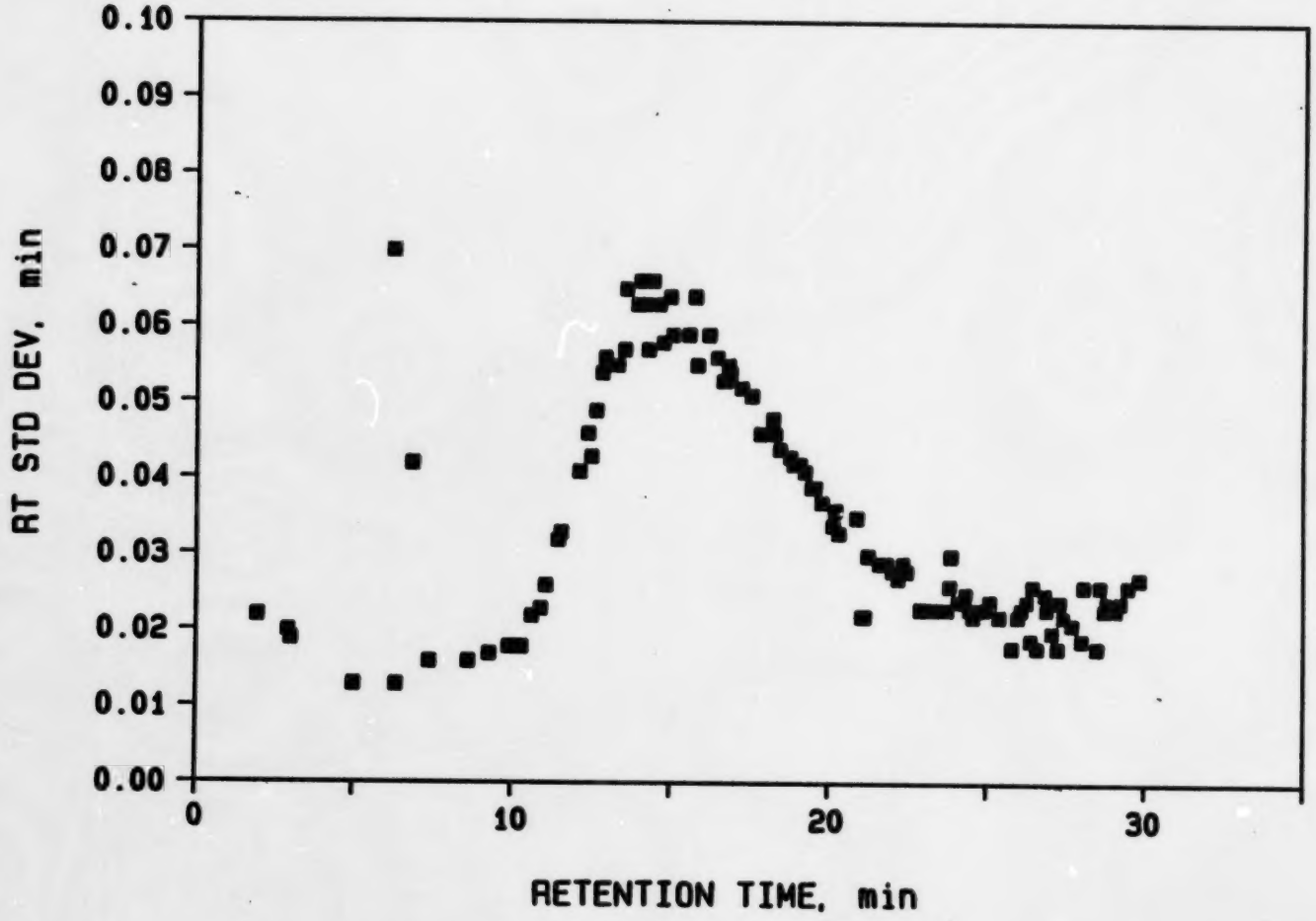


FIGURE 1. TYPICAL C_2 TO C_{12} CAPILLARY COLUMN/FID CHROMATOGRAM OF URBAN AIR.



88-150.8

Figure 2. Retention time precision versus retention time.